CURE BEHAVIOR AND MECHANICAL PROPERTIES OF GRAPHENE/EPOXY NANOCOMPOSITES

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Thermosetting epoxy polymers are widely used in many applications such as adhesives, coatings and matrices of composite materials due to their good characteristics: chemical and solvent resistance, thermal and mechanical properties, high creep resistance, low shrinkage on curing and excellent adhesion to metals and ceramic materials.

Since the discovery of graphene nanoplatelets (GNPs) their use as nanofiller of polymers has taken great interest because graphene could bring many benefits such as increase of mechanical properties and thermal conductivity of the matrix, enhance of the thermal and hydrothermal resistance, obtain electrically conductor composites, increase the hydrophobic character of the composite surfaces, increase the microwave absorption… Moreover the use of GNPs as polymer reinforcement has the advantage of their low cost regarding to the use of carbon nanotubes, due to their lower manufacturing cost.

Most of the studies of polymer-graphene nanocomposites deal with the processing methods of these composites in order to get nanoplateles well dispersed in the polymer matrix that assure the improvement of their properties (1-2).

As the curing process of the matrix is critical in defining the material properties of epoxy composites, it would be interesting to explore the influence of GNPs on the curing of graphene-epoxy dispersions.

In this work we study the curing process of an epoxy resin reinforced with graphene nanoplatelets and the thermal and mechanical properties of the obtained nanocomposites, in order to clarify the effect of GNPs on these properties.

Experimental

Graphene nanoplatelets (GNPs) were supplied by XGScience, with the commercial name of M25, with average flake thickness 6 nm and the average lateral particle size 25 μm. The epoxy monomer was Diglycidyl Ether of Bisphenol A (DGEBA) (Araldite F, Ciba). The curing agent was 4,4'-diamino diphenylmethane (DDM) (Acros Organics). Stoichiometric ratio of DGEBA to DDM was used to prepare all the samples.

Dispersions of GNPs in the DGEBA resin were prepared with two different concentrations: 1 and 5% w/w. The followed procedure was: thermal agitation (0.5h) and sonication (1h). Once the dispersions were prepared, they were studied by differential scanning calorimetry (DSC) in order to investigate the curing reaction. All the samples were scanned 3 times in the DSC instrument. The temperature of the exothermic peak (T_{peak}) and the reaction enthalpy (ΔH) were obtained from the first scan (-50 to 320ºC). First scans were performed at different heat rates (5 to 30ºC / min) in order to obtain the apparent activation energy of the cure reaction (E_a). The second and third scans from 25 to 250ºC were performed at 10° C/min, with the aim of obtaining the T_g of the nanocomposite formed during the first scan.

The results were compared with those of neat thermoset DGEBA-DDM ones. Moreover samples cured in an oven (2h at 120ºC + 1h at 180ºC) were prepared for dynamic mechanical thermal analysis (DMTA) and for tensile stress-strain measurements. DMTA measurements of epoxy-GNPs cured nanocomposites and of the neat epoxy thermoset were carried out from 30 to 220ºC at 0, 1, 2, 5, 10 and 50 Hz.

Results and Discussion

Tabla 1 shows the DSC results obtained for the curing of two GNPs dispersions on DGEBA-DDM during the and for the neat DGEBA-DDM (T_{peak}, ΔH *and* E_a) together with the T_g values of the obtained nanocomposite.

Table 1. DSC results: T_{peak} obtained at 10ºC/min, ΔH **(**mean values for the different heating rates), T_g from the second and third DSC scan and E_a.

Sample	T_{peak} **(ºC)**	$-\Delta H$ **(kJ/g epoxy)**	T_g **(ºC)** from 2nd scan	T_g (ºC) from 3rd scan	E_a***(KJ/mol)***
DGEBA-DDM	163	445	155	156	56
DGEBA-DDM 1% GNP	166	422	144	145	55
DGEBA-DDM 5%GNP	154	428	146	147	56

As it can be seen in Table 1 T_{peak} value for DGEBA-DDM 5% GNP is lower than the corresponding value of DGEBA-DDM, this means that the curing reaction is accelerated in the presence of graphene, however this catalytic effect is imperceptible for samples with very low graphene content (1%). The heat of reaction, ΔH, for each composition is almost independent of the heating rate, thus the values shown in Table 1 are the mean values from the six heating rates measured for each composition. The presence of graphene lowers ΔH this means that the epoxy matrix in the nanocomposites has lower crosslinking degree than in neat DGEBA-DDM. This can suggest that graphene hinders the reaction of epoxy groups leading to a less perfect network than neat DGEBA-DDM. This agrees with the T_g values of the cured samples, that are lower for the nanocomposites than for neat epoxy thermoset (see Table 1). Table 1 also shows the apparent activation energy of the curing reaction obtained from the slope of the Arrhenius plot (ln heat rate vs. T_{peak}^{-1}) for each sample, as it can be seen there are not significant variation of E_a due to the presence of GNPs.

Table 2 shows the values of storage modulus, E', relative to neat DGEBA-DDM ($E'_{relative} = E'_{sample}/E'_{DGEBA-DDM}$) in the glassy region ($T < T_g$) and in the rubbery region ($T > T_g$) and the temperature of *tan*δ peak (α-relaxation associated to the glass transition) at 1 Hz. The nanocomposites with 5% of GNPs present an increased glassy modulus and rubbery modulus with regard to neat epoxy resin, being the increment 30% at 50ºC and 70% at 190ºC. The higher glassy and rubbery moduli are correlated with stronger interactions between the nanofiller and the epoxy matrix, while the lower tanδ peak indicates a lower crosslinking density and a higher mobility of the polymer chains. However for the nanocomposite containing 1% GNPs the increase of E' is imperceptible, the differences with the corresponding values of the neat epoxy thermoset are within the experimental error.

Table 2 also shows the T_g obtained from DSC for these samples. As usual the T_gs from DSC are lower than the temperature of $\tan\delta_{peak}$ at 1Hz. Comparing the T_gs of the samples cured in an oven (2h 120ºC + 1h 180ºC) given in Table 2 with the T_gs of the samples cured during the first DSC scan (Table1), it can be concluded that the isothermal protocol of curing leads to more perfect network structures than the dynamic curing in the DSC.

Table 2. DMTA results at 1Hz: storage modulus in the glassy (E_G') and rubbery (E_R') regions and $\tan\delta_{peak}$

Sample	$\mathbf{E'_{relative}}$ (50ºC, glassy)	$\mathbf{E'_{relative}}$ (50ºC, rubbery)	$\mathbf{\tan\delta_{peak}}$ **(ºC)**	***Tg*** from DSC **(ºC)**
DGEBA-DDM	1.0	1.0	172	162
DGEBA-DDM 1% GNP	1.0	1,0	171	162
DGEBA-DDM 5%GNP	1.3	1,7	168	158

The tensile properties: tensile modulus, tensile strength (stress at break) and strain at break of the nanocomposites and neat epoxy thermoset were determined from the stress-strain curves at room temperature (22 ºC, glassy state). The tensile results, which represent average values from 6-7 tests, are given in Table 3. The most significant effect of GNPs is the increase of the Young modulus of the composite: increases of 10% for 1%GNP and 28% for 5% GNP. However for high GNP content (5%) there is a decrease of tensile strength and strain at break

Table 3. Stress-strain results from tensile experiments

Sample	**Tensile modulus** (GPa)	**Tensile strength** (MPa)	**Strain at break** (%)
DGEBA-DDM	2.50±0.08	69±2	4.4±0.4
DGEBA-DDM 1% GNP	2.74±0.06	71±2	4.5±0.5
DGEBA-DDM 5%GNP	3.2±0.15	42±5	2.0±0.4

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